Photodissociation of O₃ around 309 nm

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Abstract

Photodissociation reaction of O₃ following ultraviolet photon excitation around the thermodynamic threshold of the dissociation channel of \( \text{O}^\dagger(\text{D}) + \text{O}_2(a^\dagger \Delta_g) \) at 309.44 nm has been studied under room-temperature and jet-cooled conditions. Both O\(^\dagger\)(D) and O\(^3\)(P) photoproducts are detected by a technique of vacuum ultraviolet laser-induced fluorescence (vuv-LIF) spectroscopy. Photofragment excitation (PHOFEX) spectra for the O\(^\dagger\)(D) and O\(^3\)(P) atoms are obtained by scanning the photolysis laser wavelength between 297 - 316 nm while monitoring vuv-LIF signal intensities at 115 nm and 130 nm for O\(^\dagger\)(D) and O\(^3\)(P), respectively. From the behavior of the PHOFEX spectra for the O\(^3\)(P) and O\(^\dagger\)(D) atoms around the threshold into O\(^\dagger\)(D) + O\(_2(a^\dagger \Delta_g)\), the existence of an exit barrier along the O-O\(_2\) dissociation coordinate in the photoexcited electronic state of O₃ is suggested. Analysis of the linewidths in the jet-cooled PHOFEX spectra of O\(^\dagger\)(D) and O\(^3\)(P) suggests that the quasi-bound states below the barrier and above the threshold have lifetimes of 0.2 - 0.8 ps. The O\(^\dagger\)(D) quantum yield values from the O photolysis are obtained from the PHOFEX spectrum for O\(^3\)(P) at 295 K. The O\(^\dagger\)(D) quantum yields between 297
and 305 nm are almost independent of the photolysis wavelength (≈ 0.89), which is smaller than the current NASA/JPL recommendation for atmospheric modeling (0.95). The physical model for O(\(^{1}\)D) formation in the photolysis of O\(_{3}\) in the wavelength range of 305 - 329 nm is presented, which can quantitatively explain the temperature and wavelength dependence of O(\(^{1}\)D) quantum yield.
Introduction

The photodissociation reaction of O₃ following photoexcitation by solar ultraviolet (uv) radiation plays a key role in atmospheric chemistry and its importance has motivated a lot of experimental and theoretical studies. Photoabsorption of O₃ in the ultraviolet region consists of two bands: the wide bell-shaped absorption peaked at around 250 nm is called Hartley band, while a vibrational structure in the long wavelength edge of Hartley band in the 310-360 nm region is called Huggins band. Figure 1 shows a schematic diagram of the intersections for the O₃ potential energy surfaces (PESs) as a function of the bond length for one of the O-O bonds. The Hartley band is attributed to the transitions onto the saddle-geometry region of the electronically excited ¹B₂ PES corresponding to ground state equilibrium configurations with strong Franck-Condon (FC) overlap (Fig. 1). The origin of the Huggins band has been the subject of controversial discussions and there are two explanations. One is that the Huggins band structure is attributed to the transitions to some bound states on the excited ¹B₂ PES displaying small FC overlaps with the ground state, so that the Huggins band comes from the same transition as the Hartley band. The other is the transition to the ²A₁ PES, and small cross sections are due to its orbitally forbidden character. The potential curve for the ²A₁ state is not depicted in Fig. 1.

The uv ozone photolysis in the wavelength region around 300 - 330 nm can proceed via five energetically allowed channels,

\[ O_3 + h\nu (\lambda < 309 \text{ nm}) \rightarrow O(¹D) + O_2(a'Δ_g) \]  \hspace{1cm} (1)
\[ O_3 + h\nu (\lambda < 1180 \text{ nm}) \rightarrow O(³P) + O_2(Χ²Σ^-_g) \]  \hspace{1cm} (2)
\[ O_3 + h\nu (\lambda < 411 \text{ nm}) \rightarrow O(¹D) + O_2(Χ²Σ^-_g) \]  \hspace{1cm} (3)
\[ O_3 + h\nu (\lambda < 463 \text{ nm}) \rightarrow O(³P) + O_2(b'Σ^+_g) \]  \hspace{1cm} (4)
\[ O_3 + h\nu (\lambda < 612 \text{ nm}) \rightarrow O(³P) + O_2(a'Δ_g) \]  \hspace{1cm} (5)
where wavelengths given in parentheses indicate the thermodynamic cut-off for each channel. Recent experimental studies \(^{15-26}\) confirmed that not only the spin-allowed channels (1) and (2) which are predominant in the Hartley band but also spin-forbidden channels (3) - (5) occur in the Huggins band. When ozone is photoexcited in the Hartley band at \(\lambda < 309\) nm, the excited state \((^1B_2)\) gives rise to channel (1) dissociation, while the potential crossing between the \(^1B_2\) and \(R\) states leads to channel (2) dissociation (see Fig.1). The experimental studies \(^{15,21}\) at wavelengths longer than about 320 nm suggested that the channel (3) products are formed as a result of the crossing of the singlet exit channel, which leads to the channel (2) products, by triplet states correlating with the channel (3) products. Theoretical studies about the \(O_3\) triplet states correlating to the spin-forbidden products (3) - (5) have not been carried out. The inferred triplet state which is responsible for the channel (3) products is schematically depicted by a broken curve in Fig.1.

Among the photoproducts from the uv photolysis of \(O_3\), the \(O(^1D)\) atom plays active and ubiquitous roles in the photochemical processes of the Earth’s atmosphere \(^1,2\). Much attention has been paid into the wavelength and temperature dependence of the quantum yield of the \(O(^1D)\) formation from the \(O_3\) photolysis at around 315 nm, since it is very important to evaluate the oxidative capacity in the troposphere and lower stratosphere. Numerous previous studies indicated that channel (1) is predominant at wavelengths \(\lambda < 306\) nm and the \(O(^1D)\) quantum yield is almost independent of the photolysis wavelength, with a reported quantum yield of 0.9 - 0.95 throughout the Hartley band \(^3\). For \(\lambda > 306\) nm, the \(O(^1D)\) quantum yield decreases sharply with increasing the photolysis wavelength \(\lambda\) \(^{16,18,20,23}\), since the energetic threshold for channel (1) lies at 309.44 \(\pm\) 0.03 nm \(^{26}\). Even below the energetic threshold into channel (1), the \(O(^1D)\) quantum yield does not simply reach to zero. This is because there are other processes to produce \(O(^1D)\) atoms even at \(\lambda >\)
309.44 nm. Between 309 and ca. 320 nm, the O(^1D) atoms arise predominantly from the photodissociation of vibrationally excited O_3 molecules which are thermally populated under atmospheric conditions. Takahashi et al.\textsuperscript{15} pointed out that prior excitation in the asymmetric stretching (ν_3) vibration extensively promotes the photoabsorption, which results in the fragmentation into O(^1D) + O_2(a^1Δ_g) through channel (1). The high effectiveness of the ν_3 mode in the hot band excitation was explained by the large enhancement of the Franck-Condon factors between the photoexcited 1B_2 state and the ν_3 excited levels in the ground electronic state. Theoretical calculations on the O_3 PESs indicate that the energetically minimum point in the ground electronic state is located at an equal length position for the two O-O bonds, while the 1B_2 photoexcited state has minimum points at unequal length positions.\textsuperscript{8,10,12,13} In the wavelength region of λ > ca. 320 nm, the formation of O(^1D) does not result predominantly from the hot band excitation but from the spin-forbidden dissociation channel (3)\textsuperscript{15-23}. Although the quantum yield of O(^1D) from channel (3) is small (≈ 0.06 - 0.08\textsuperscript{20-23}), its contribution has a great impact on the O(^1D) production rate in atmospheric chemistry\textsuperscript{22,23}.

Based on the laboratory studies on the O_3 photolysis in the near uv region, mathematical expressions for the O(^1D) quantum yield as functions of photolysis wavelength and temperature have been proposed for application to atmospheric modeling. The NASA/JPL recommendation\textsuperscript{27} adopted the formulation presented by Michelsen et al.\textsuperscript{28} Recent experimental studies have verified that the NASA/JPL recommendation underestimates the atmospheric O(^1D) production yield, especially at the longer photolysis wavelengths (λ > 320 nm). The discrepancy is attributable to contribution from the O(^1D) atoms generated via the spin-forbidden channel (2), which is not included in the current NASA/JPL recommendation. Talukdar et al.\textsuperscript{22} suggested a model to calculate the O(^1D) yield, Φ(λ,T) at wavelength λ and at temperature T, using an analytical function: 


\[ \Phi(\lambda, T) = 0.06 + A_\lambda \exp\left( -\frac{B_\lambda}{T} \right), \] (6)

where \( A_\lambda \) and \( B_\lambda \) are the wavelength dependent constants. In Eq. (6) the offset of 0.06 corresponds to the contribution of the spin-forbidden channel (3), which is not included in the NASA/JPL formulation\(^{27}\).

In this paper, we report experimental studies on the formation processes of \( \text{O}^3\text{P} \) and \( \text{O}^1\text{D} \) atoms from photolysis of \( \text{O}_3 \) around 309 nm under room-temperature and jet-cooled conditions. The PHOFEX spectra are measured by scanning the photolysis laser wavelength while monitoring vuv-LIF intensities at 115 nm and 130 nm for \( \text{O}^1\text{D} \) and \( \text{O}^3\text{P} \), respectively. The existence of an exit barrier along the \( \text{O}-\text{O}_2 \) bond breaking direction on the PES of the photoexcited \( ^1\text{B}_2 \) state of \( \text{O}_3 \) is suggested from the analysis of the PHOFEX spectra near the thermodynamic threshold for channel (1) at 309.44 nm. The \( \text{O}^1\text{D} \) quantum yields in the wavelength range of 296 - 312 nm are obtained from the room-temperature PHOFEX spectrum for \( \text{O}^3\text{P} \). A new numerical model to explain the mechanism and the quantum yield values for \( \text{O}^1\text{D} \) formation from the photolysis of \( \text{O}_3 \) in the wavelength range 305 - 329 nm has been presented.

**Experimental**

The experimental apparatus used to study ozone photochemistry in our laboratory has been described in detail elsewhere\(^{16}\) and we give only brief description pertinent to the current study here. \( \text{O}_3 \) was prepared by passing ultra-pure \( \text{O}_2 \) (Nihon Sanso, 99.9995%) through a commercial ozonizer and collected on silica gel at a liquid nitrogen/methanol slush temperature (ca. 175 K). Once sufficient \( \text{O}_3 \) was produced, residual gas was pumped away and the ozone desorbed into a blackened storage glass bulb. Ozone photolysis was performed a) under conditions of substantial cooling in a pulsed expansion and b) under flow conditions at room temperature (295 K). In the supersonic jet
experiments, a gas mixture (typically 2-3 % O$_3$ in He, at a total pressure of ca. 1000 Torr, 1 Torr = 133.3 Pa) was injected through a pulsed nozzle (General Valve, Series 9, hole dia. 0.8 mm) into the stainless steel vacuum chamber, evacuated by a liquid-nitrogen trapped oil diffusion pump. During the experiments, typical background pressure in the vacuum chamber was $1 \times 10^{-4}$ Torr when the pulsed nozzle was operated at a repetition rate of 10 Hz with a duration of 230 $\mu$s. In the flow cell experiments, a mixture of O$_3$ (1 %) in Helium gases was slowly flowed into a photodissociation cell which was pumped by a rotary pump (330 l/min) through a liquid nitrogen trap. The total pressure in the flow cell was maintained at 1 Torr.

The O$_3$ molecules were photolyzed by the tunable laser light in the wavelength range of 297 - 316 nm, which was generated by a Nd:YAG pumped dye laser (Lambda Physik, Scanmate 2EC-400) with a second harmonics generation crystal (KD*P). The typical photolysis laser pulse energies were 0.5 mJ. The wavelength of the fundamental visible light was calibrated by simultaneously measuring the laser-induced fluorescence excitation spectrum of iodine vapor with published chart 29.

The O($^3P$) photofragments from O$_3$ were detected by vuv-LIF method for the 3s $^3S$ - 2p $^3P_j$ transition at 130.22 nm for $j = 2$, 130.48 nm for $j = 1$, and 130.60 nm for $j = 0$. The vuv laser around 130 nm was generated by four-wave difference mixing ($2\omega_1 - \omega_2$) in krypton gas 30, using two dye lasers simultaneously pumped by a XeCl excimer laser (Lambda Physik FL3002’s and Lextra-50). Typical pressure of the Kr gas in the mixing cell was 15 Torr. The dye laser output (Bis-MSB laser dye in 1,4-dioxane) was frequency-doubled by a BBO crystal for $\omega_1$ wavelength of 212.56 nm, which was two-photon resonant with Kr 5p[1/2]$_0$. The wavelength of $\omega_2$ (Coumarin 540A in methanol) was around 578.1, 572.8, and 570.6 nm for $j = 2$, 1, and 0, respectively.

For the detection of the O($^1D$) photofragments from O$_3$ photolysis, the probe laser system was rearranged to observe the vuv-LIF of the 3s $^1D$ - 2p $^1D$ transition at 115.22 nm. The 115.22 nm laser light was generated by phase-matched frequency tripling of the output from a dye laser at
345.6 nm in Xe (40 Torr) / Ar (120 Torr) gas mixture. The dye laser pumped by the XeCl excimer laser was used with PTP dye solution to generate the 345.6 nm light (~ 5 mJ / pulse incident laser intensity). The laser beam(s) for the four-wave mixing or the frequency tripling were focused with a lens (f = 200 mm) into the Kr or Xe/Ar containing cell. The generated vuv laser light was introduced into the reaction chamber through a LiF window. The bandwidth of the 115 nm vuv radiation was estimated to be 0.65 cm$^{-1}$ (FWHM).

The photolysis and probe laser pulses were counter-propagated and separated in time by 100 ns using a pulse delay controller (Stanford Research, DG535). The vuv-LIF signals associated with both the O($^1$D) and the O($^3$P) photoproducts were detected along the vertical direction, orthogonal to propagation direction of both vuv probe and photolysis laser beams, using a solar-blind photomultiplier tube (EMR, 541J-08-17). The output from the photomultiplier was recorded using a boxcar (Stanford Research, SR-250) and stored on a pc. The signal intensity in the PHOFEX spectra was corrected to the intensity of the vuv laser by recording the photo-ionization current from a sample of NO contained (typically 2 Torr) within a cell with lithium fluoride windows located after the main vacuum chamber.

**Results**

Figure 2 shows the photofragment excitation (PHOFEX) spectrum for O($^3$P) atoms produced in the photodissociation of O$_3$ under room temperature conditions (295 K). For measurements of the PHOFEX spectrum, the wavelength of the vuv probe laser was fixed to the center of the 3s $^3$S$^o$-2p $^3$P$_2$ resonance line at 130.22 nm for O($^3$P$_2$), while the wavelength of the uv photolysis laser was continuously scanned between 297 and 314 nm. Two factors should be considered to verify that the obtained PHOFEX spectrum for O($^3$P$_2$) is proportional to the total O($^3$P$_j$, j=0, 1 and 2) yield in the photolysis of O$_3$: one is the Doppler profiles of O($^3$P$_j$) fragments and the other is the fine structure branching ratio (j-distribution) among the spin-orbit levels of the
$O(^3P_j)$ fragments. The linewidth of the vuv probe laser light (~0.83 cm$^{-1}$) is narrower than the Doppler spectral width of the nascent $O(^3P)$ fragments. If the Doppler width of the nascent $O(^3P)$ were strongly dependent on the photolysis wavelength, the PHOFEX spectrum might not be proportional to the $O(^3P_j)$ yield spectrum. The width of the $O(^3P_j)$ Doppler line shapes was found to be independent of the photolysis wavelength and remained almost constant value (1.05 cm$^{-1}$).

No obvious variation in linewidth was discernible over the photolysis wavelength range 297 - 314 nm. This is reasonable because the spin-allowed dissociation process of channel (2) is predominant and the $O(^3P)$ formation via the spin-forbidden channels (4) and (5) is very small in this wavelength range$^{21}$. We also measured the branching ratios among the $j$-levels of the $O(^3P_j)$ atoms produced from the $O_3$ photolysis at several photolysis wavelengths. The results obtained for the $j$-branching are listed in Table I. The $j$-branching remained almost constant in the wavelength range 297 - 316 nm, and were in good agreement with the previous reports$^{16,21,32}$. Thus, these measurements confirmed that the PHOFEX spectrum for the $O(^3P_j)$ fragments in Fig. 2 is proportional to the total yield spectrum for $O(^3P_j)$.

Figure 3 shows the PHOFEX spectra for $O(^1D)$ and $O(^3P)$ fragments produced in the photodissociation of $O_3$ under jet-cooled and 295 K conditions. For measurements of the $O(^1D)$ PHOFEX spectra, the wavelength of the vuv probe laser was fixed to the center of the 3s $^1D_o$ - 2p $^1D$ resonance line at 115.22 nm for $O(^1D)$, while the wavelength of the uv photolysis laser was continuously scanned. The invariance of the linewidths of $O(^1D)$ in the wavelength range of Fig. 3 was also checked to ensure that the PHOFEX spectrum was proportional to the yield spectrum of $O(^1D)$. The linewidth of the nascent $O(^1D)$ fragments from $O_3$ photolysis at room temperature was also found to be independent of the photolysis wavelength (0.67 cm$^{-1}$). This implies that the $O(^1D)$ atoms probed are predominantly produced via channel (1), since $O_3$ is photolyzed around the channel (1) threshold and the resultant $O(^1D)$ fragments can have only a little translational energy.
The PHOFEX spectra for O(^1D) were corrected for photolysis and probe laser intensity variations. The linear dependence of the LIF signal on photolysis laser power at various photolysis wavelengths ensured that the O(^1D) atoms come from one-photon dissociation of parent O_3. Thus, the O(^1D) PHOFEX spectrum shown in Fig.3 can quantitatively reflect the relative yield of the O(^1D) production.

The free-jet experiments were carried out with several different O_3/He mixing ratios in expansion gas (1 - 6 %) and under different stagnation pressure conditions (700 - 1100 Torr). The PHOFEX spectra obtained were dependent neither on the O_3 concentration in the expansion gas nor on the stagnation pressure. This indicates that van der Waals complex or dimer molecules do not affect the PHOFEX spectra for O(^1D) and O(^3P) atoms. To estimate the rotational temperature of O_3 in the supersonic jets, the LIF spectrum of carbon monoxide (CO) was measured around 115 nm under the same jet conditions. The rotational lines associated with the (0,0) band of the electronic transition B^1Σ^+ - X^1Σ^+ were recorded. Analysis of the spectra revealed that the rotational populations were well reproduced by a Boltzmann distribution at a rotational temperature of T_rot = 3 K. Similar rotational cooling should be achieved in the O_3 experiment.

As shown in Fig.3, the O(^1D) yield in the supersonic beam decreases as the photolysis wavelength increases and a clear cut-off for the O(^1D) formation appears at 309.44 nm. The cut-off wavelength corresponds to an appearance potential of the dissociation path into O(^1D) + O_2(a^3Δ_g) (channel (1)) which is indicated by a broken line. Accordingly the signal intensity of the O(^1D) drastically changes at the threshold wavelength. A small amount of the O(^1D) formation at λ > 309.44 nm is attributed to the vibrationally hot-band excitation of the parent O_3 molecules. Under the supersonic free-jet conditions, the vibrational cooling of the parent molecules is less efficient than the rotational cooling. On the other hand, such a cut-off is not clearly identified in the room temperature PHOFEX spectrum for O(^1D). This is due to contribution from the photolysis of
rotationally excited O\textsubscript{3} in the thermal sample. As shown in the Fig.3, the spectral features are more resolved in the jet-cooled spectra than those at 295 K for both of the O(\textsuperscript{1}D) and O(\textsuperscript{3}P). These aspects indicate that the spectral broadening at 295 K is due to the overlaps of rotational envelopes among the vibrational bands.

Figure 4 shows the detailed PHOFEX spectra for O(\textsuperscript{1}D) and O(\textsuperscript{3}P) atoms between 306 nm and 310 nm taken under jet-cooled conditions. In both spectra, sharp peaks are discernible. The structures resemble to each other between the O(\textsuperscript{1}D) and O(\textsuperscript{3}P) spectra, although the contributions of the background continuum are different. The linewidths of the sharp peaks are measured to be in the range of 7-35 cm\textsuperscript{-1} in FWHM, which correspond to the lifetimes of 0.2 – 0.8 ps by the uncertainty principle. The photoabsorption spectrum for O at 218 K\textsuperscript{7} was also shown for comparison.

Figure 5 shows the quantum yield of O(\textsuperscript{1}D) formation from the uv photolysis of O\textsubscript{3} at 295 K, as a function of the photolysis wavelength between 296 and 314 nm. The quantum yield spectrum for O(\textsuperscript{1}D) production shown in Fig. 5 is calculated by Eq. (7);

\[
\Phi_{1D}(\tilde{\varepsilon}) = \frac{\dot{\sigma}_{1D}(\tilde{\varepsilon})}{\dot{\sigma}_{abs}(\tilde{\varepsilon})} = 1 - \frac{\dot{\sigma}_{3P}(\tilde{\varepsilon})}{\dot{\sigma}_{abs}(\lambda)} = 1 - \frac{s_{3P} \times Y_{3P}(\tilde{\varepsilon})}{\dot{\sigma}_{abs}(\tilde{\varepsilon})}, \tag{7}
\]

where \(\Phi_{1D}(\lambda)\) is the O(\textsuperscript{1}D) quantum yield at a photolysis wavelength \(\lambda\), \(\sigma_{abs}(\lambda)\) is the total absorption cross section of O\textsubscript{3}, \(\sigma_{1D}(\lambda)\) and \(\sigma_{3P}(\lambda)\) are the partial cross sections for O(\textsuperscript{1}D) and O(\textsuperscript{3}P) formation, respectively, and \(Y_{3P}(\lambda)\) is the PHOFEX spectrum for O(\textsuperscript{3}P) recorded at room temperature. \(s_{3P}\) represents the sensitivity factor in the O(\textsuperscript{3}P) detection. In the wavelength range shown in Fig. 5 only the two states of O atoms can be produced from the photolysis of O\textsubscript{3}, that is, \(\sigma_{abs}(\lambda) = \sigma_{1D}(\lambda) + \sigma_{3P}(\lambda)\). The absorption cross sections of O\textsubscript{3} reported by Malicet \textit{et al.}\textsuperscript{7} are used as \(\sigma_{abs}(\lambda)\). The PHOFEX spectrum for O(\textsuperscript{3}P) at 295 K in Fig. 2 is proportional to the partial cross-section spectrum, that is \(\sigma_{3P}(\lambda) = s_{3P} \times Y_{3P}(\lambda)\). Since the vertical scale of the O(\textsuperscript{3}P) PHOFEX
spectrum in Fig.3 is not absolute but relative, the value of coefficient $s_{3P}$ is determined so that the values of the O($^1D$) yield at 308 nm is 0.79. Several studies have indicated that the absolute O($^1D$) quantum yield is 0.79 $^{21,22,35,36}$. Our O($^1D$) quantum yields shown in Fig.5 were thus obtained in the photolysis wavelength range of 296 - 314 nm. Table II lists the O($^1D$) quantum yield values from O$_3$ photolysis at room temperature. The uncertainties of the O($^1D$) quantum yields listed in Table II come from the run-by-run fluctuations in the O($^3P$) PHOFEX spectrum measurements.

Discussion

A. Photodissociation processes of O$_3$ around the threshold into O($^1D$) + O$_2(a',\Delta_g)$

The cut-off wavelength in the O($^1D$) PHOFEX spectrum of jet-cooled O$_3$ (Fig. 3) corresponds to the energetic threshold into channel (1). The threshold energy of channel (1) has been measured to be 309.44 ± 0.03 nm $^{26}$. The quantum yield spectrum for O($^1D$) production from O$_3$ photolysis in Fig. 5 indicates a marked fall-off at $\lambda = 306$ nm. Many studies on the O($^1D$) quantum yield have shown that the O($^1D$) quantum yield starts to decline at $\lambda = 306$ nm $^{1-3,18,20-23}$. It has been thought that the decrease of the O($^1D$) quantum yield towards the longer photolysis wavelength should be due to the thermochemical threshold for formation of O($^1D$) via channel (1). However, the exact threshold wavelength for it has been measured to be 309.44 ± 0.03 nm $^{26}$. Therefore, the wavelength of 306 nm where the marked fall-off is observed in the O($^1D$) quantum yield spectrum is shorter than that of the exact channel (1) threshold. There has been no explanation about the "early decrease" of the O($^1D$) formation at wavelengths shorter than the exact threshold. Photolysis of the internally excited O$_3$ molecules cannot explain the early decrease of the O($^1D$) formation at wavelengths shorter than the threshold, although it can explain the formation of O($^1D$) at wavelengths longer than the threshold $^{15-23,28}$. 
The sum of quantum yields for $\text{O}(^3\text{P})$ and $\text{O}(^1\text{D})$ must be unity at wavelengths $\lambda > 237$ nm, in which the wavelength is the thermochemical threshold for channel of $\text{O}(^1\text{S}) + \text{O}(X^3\Sigma_g^-)$. The jet-cooled PHOFEX spectrum for $\text{O}(^1\text{D})$ shows the clear cut-off at the channel (1) threshold of 309.44 nm, as shown in Fig. 3. At the wavelengths longer than the threshold of 309.44 nm, photoexcited $\text{O}_1$ molecules mainly dissociate into channel (2) by changing the surface from the photoprepared $^1\text{B}_2$ state to the R state (see Fig. 1). When the photon energy exceeds the channel (1) threshold, the direct dissociation path to $\text{O}(^1\text{D}) + \text{O}_2(a^1\Delta_g)$ is opened in the photoexcited state. Therefore, a sudden decrease of the $\text{O}(^3\text{P})$ formation yield is expected at the channel (1) threshold, since the direct dissociation to the $\text{O}(^1\text{D}) + \text{O}_2(a^1\Delta_g)$ products should be more efficient than the potential switching to form the $\text{O}(^3\text{P}) + \text{O}_2(X^3\Sigma_g^-)$ products. However, the PHOFEX spectra for $\text{O}(^3\text{P})$ atoms under 295 K and jet-cooled conditions does not show such a sudden decrease at the shorter wavelength side of the threshold. Both of the $\text{O}(^3\text{P})$ PHOFEX spectra show gradual decrease from the threshold (309.44 nm) toward the shorter wavelength and then have minima around 306 nm, as shown in Fig.3. The considerable formation of $\text{O}(^3\text{P})$ atoms between 306 and 309.44 nm in Fig. 3 is responsible for the early decrease of the $\text{O}(^1\text{D})$ quantum yield spectrum shown in Fig. 5. The product branching between the $\text{O}(^1\text{D})$ and $\text{O}(^3\text{P})$ atoms is decided by the dissociation rates to each product. The early decrease in the $\text{O}(^1\text{D})$ quantum yield spectrum between 306 and 309.44 nm indicates that the dissociation rate to $\text{O}(^1\text{D}) + \text{O}_2(a^1\Delta_g)$ [channel (1)] at those wavelengths is suppressed or that the dissociation rate to $\text{O}(^3\text{P}) + \text{O}_2(X^3\Sigma_g^-)$ [channel (3)] is enhanced.

The early decrease in the $\text{O}(^1\text{D})$ quantum yield spectrum can be interpreted by the presence of an exit barrier on the $^1\text{B}_2$ photoexcited state surface along the bond breaking coordinate into $\text{O}(^1\text{D}) + \text{O}_2(a^1\Delta_g)$. The exit barrier can reduce the rate of direct dissociation of $\text{O}_3(^1\text{B}_2)$ into $\text{O}(^1\text{D}) + \text{O}_2(a^1\Delta_g)$, when the excitation energy is below the barrier top. Existence of the exit barrier
has also been suggested by theoretical calculations \textsuperscript{10,13,37}. The measured O(\textsuperscript{1}D) PHOFEX spectrum under jet-cooled conditions shown in Fig. 3 supports the existence of the barrier. The jet-cooled PHOFEX spectrum for O(\textsuperscript{1}D) shows sharp structure in the range of $306 < \lambda < 309.44$ nm, while it exhibits broad features at $\lambda < 306$ nm. The broad features at $\lambda < 306$ nm may be attributed to the bound-free transition, that is, O\textsubscript{3} molecules are excited to the repulsive part of the $^1B_2$ state above the barrier top. They dissociate predominantly into O(\textsuperscript{1}D) + O(\textsuperscript{a}1\Delta\textsubscript{g}) quickly. On the other hand, the sharp structure in the jet-cooled PHOFEX spectrum for O(\textsuperscript{1}D) in the range of $306 < \lambda < 309.44$ nm is caused by long lifetimes in the upper state. This is due to the transitions onto quasi-bound states below the exit barrier top in the $^1B_2$ surface. The linewidths (FWHM) of the peaks in this wavelength range in the jet cooled PHOFEX spectrum of O(\textsuperscript{1}D) (Fig. 4) are in the range of $7 - 35$ cm\textsuperscript{-1}, which correspond to the lifetimes of 0.2 – 0.8 ps. The sharpest peak observed at 309.1 nm has the linewidth of 7 cm\textsuperscript{-1} in FWHM, the value of which is as small as the rotational broadenings of the structural peaks in the jet-cooled PHOFEX spectrum for O(\textsuperscript{1}D) generated from the Huggins band photolysis of O\textsubscript{3} at $321 < \lambda < 328$ nm which is below the threshold to O(\textsuperscript{1}D) + O\textsubscript{2}(\textsuperscript{a}1\Delta\textsubscript{g}) under jet-cooled conditions \textsuperscript{15}.

The formation of O(\textsuperscript{1}D) atoms is still observed even when the O\textsubscript{3} molecule is excited to the quasi-bound state below the exit barrier on the $^1B_2$ PES between 306 and 309.44 nm. The O\textsubscript{3} molecule in the quasi-bound levels in the $^1B_2$ state may change its potential surface to another electronic state surface which leads to O(\textsuperscript{1}D) + O(\textsuperscript{a}1\Delta\textsubscript{g}) fragmentation without any barrier in the exit channel, and also change surfaces to the R surface which leads to O(\textsuperscript{3}P) + O\textsubscript{2}(X\Sigma\textsubscript{g}^-) fragmentation (see Fig.1). There are nine states correlating to channel (1) other than the $^1B_2$ state. However, the studies about them have been well performed neither theoretically nor experimentally. The rates of the crossings from the $^1B_2$ state to the two different states compete with each other in the quasi-bound states below the barrier. The barrier height is estimated to be about 400 cm\textsuperscript{-1} from
the energy difference between 306 and 309.44 nm. Theoretical studies on the \( \mathrm{O}_3( ^1 \text{B}_2) \) PES also predicted the exit barrier to the \( \text{O}(^1 \text{D}) + \text{O}_2( ^1 \Delta_g) \) products. Leforestier et al.\[36\] carried out the \textit{ab-initio} calculations for the \( \mathrm{O}_3( ^1 \text{B}_2) \) PES and showed that the surface has the exit barrier along the O-O\(_2\) bond breaking coordinate. The barrier height from the dissociation limit into \( \text{O}(^1 \text{D}) + \text{O}_2( ^1 \Delta_g) \) was calculated to be about 1550 cm\(^{-1}\). The value predicted theoretically is larger than that reported here.

In the wavelength region of \( \lambda < 306 \) nm, it is interesting that the spectral features of the two jet-cooled PHOFEX spectra for \( \text{O}(^1 \text{D}) \) and \( \text{O}(^3 \text{P}) \) are different from each other (see Fig. 3). The \( \text{O}(^1 \text{D}) \) PHOFEX spectrum has broad features in this wavelength region, while the \( \text{O}(^3 \text{P}) \) PHOFEX spectrum shows sharp peaks with high aspect ratios. This fact suggests that the upper electronic states leading to the channel (2) products have longer lifetimes than those to the channel (1) products. The initially photoprepared upper electronic states which is responsible for the both product pairs should be on the same \( ^1 \text{B}_2 \) surface. The states on the \( ^1 \text{B}_2 \) surface, which have longer lifetimes and more chances to cross the seam with the R surface, appears in the \( \text{O}(^3 \text{P}) \) PHOFEX spectrum as sharp structure. On the other hand, the states which have relatively shorter lifetimes dissociating into \( \text{O}(^1 \text{D}) + \text{O}_2( ^1 \Delta_g) \) are reflected in the \( \text{O}(^1 \text{D}) \) PHOFEX spectrum as the broad features. Detailed analysis of the vibrational structure in the jet-cooled \( \text{O}(^3 \text{P}) \) PHOFEX above the threshold wavelength will be presented in a future paper.

B. \( \text{O}(^1 \text{D}) \) quantum yield in the range of \( \lambda = 296 - 308 \) nm

Figure 5 shows the quantum yield of the \( \text{O}(^1 \text{D}) \) formation from the uv photolysis of \( \text{O}_3 \) at 295 K, as a function of the photolysis wavelength, which are obtained from the \( \text{O}(^3 \text{P}) \) PHOFEX spectrum shown in Fig. 2. In this study, the absolute values of the \( \text{O}(^1 \text{D}) \) quantum yield are determined by referring the value of 0.79 at 308 nm, as mentioned in the results. The quantum
yield spectrum between 305 and 316 nm coincides with that of the absolute measurements by Takahashi et al. They obtained the absolute O(1D) quantum yield between 305 and 328 nm by adjusting the sensitivity factors, $s_{3P}$ and $s_{1D}$, so that the sum of the PHOFEX spectra for O(3P) and O(1D), that is $Y_{3P}(\lambda)$ and $Y_{1D}(\lambda)$, fitted to the total absorption spectrum of O3, $\sigma_{ab}(\lambda)$:

$$\sigma_{ab}(\lambda) = \sigma_{1D}(\lambda) + \sigma_{3P}(\lambda) = s_{3P} \ Y_{3P}(\lambda) + s_{1D} \ Y_{1D}(\lambda) .$$  

In the eq.(8), $\sigma_{1D}(\lambda)$ and $\sigma_{3P}(\lambda)$ are the partial cross sections for producing O(1D) and O(3P) fragments, respectively. From the measurements, they reported the absolute value of the O(1D) quantum yield to be $0.79 \pm 0.12$ at 308 nm. Greenblatt and Wiesenfeld reported the value of $0.79 \pm 0.02$ for the O(1D) quantum yield from the 308 nm photolysis of O3 at 298 K. Talukdar et al. reported the value of $0.79 \pm 0.10$ at 298 K. Another study by Talukdar et al. reported the value of $0.78 \pm 0.02$ at 298 K. In these studies, the time profile of the resonance fluorescence intensity for the O(3P) products was measured by using a microwave-powered Oxygen atom lamp. The time profile was characterized by a rapid initial jump followed by a slower increase. The rapid rise is due to the direct production of O(3P), while the slower increase is to the indirect formation from the O(1D) deactivation. By analyzing the profile, the absolute quantum yields of O(1D) were obtained. The results at 308 nm from the resonance lamp experiments are in excellent agreement with that from the PHOFEX spectra measurements by Takahashi et al. In Fig. 5, the O(1D) quantum yield from the uv photolysis of O3 recommended by NASA/JPL and the experimental results measured by Talukdar et al. are also plotted for comparison. It should be noted that the O(1D) quantum yield between 297 and 305 nm obtained from the present study is
almost independent of the wavelength and is \( \sim 0.89 \) (Table II). Our results are in excellent agreement with the recent measurements by Talukdar et al.\(^{22}\) in which they reported the \( \text{O}(^3\text{P}) \) quantum yield between 289 and 305 nm is \( 0.89 \pm 0.02 \). On the other hand, the NASA/JPL recommendation \(^{27}\) is 0.95 in this photolysis wavelength range.

In the wavelength range of \( \lambda < 308 \) nm, the PHOFEX spectrum of \( \text{O}(^3\text{P}) \) reflects the change of the \( \text{O}(^1\text{D}) \) quantum yield more clearly than that of \( \text{O}(^1\text{D}) \), since the \( \text{O}(^1\text{D}) \) quantum yields are close to unity. Figure 2 shows the PHOFEX spectrum for \( \text{O}(^3\text{P}) \) at 295 K. The dotted curve drawn in Fig. 2 indicates a hypothetical spectrum of the \( \text{O}(^3\text{P}) \) PHOFEX, based on the assumption that the \( \text{O}(^1\text{D}) \) quantum yield increases from the value of 0.79 to 0.95 with decreasing the photolysis wavelength from 308 nm to 305 nm as recommended by NASA/JPL. The large difference between the actual and hypothetical spectra clearly suggests that the \( \text{O}(^1\text{D}) \) quantum yield is not as high as 0.95 at 305 nm. The \( \text{O}(^3\text{P}) \) PHOFEX spectrum between 297 and 305 nm shown in Fig. 2 is almost proportional to the absorption spectrum. This results in the almost constant behavior in the \( \text{O}(^1\text{D}) \) quantum yield spectrum between 297 and 305 nm \((\sim 0.89)\), as shown in Fig. 5.

C. Model calculations for \( \text{O}(^1\text{D}) \) production from the \( \text{O}_3 \) photolysis

Figure 6 shows the schematic diagram which indicates the contribution of the various photodissociation processes to the quantum yield spectrum for \( \text{O}(^1\text{D}) \) atoms produced from \( \text{O}_3 \) photolysis in the wavelength range of 305 - 329 nm. This diagram is taken from the paper presented by Takahashi et al.\(^{21}\) In Fig. 6, the region I indicates the contribution of the hot band excitation followed by dissociation via channel (1) at 295 K. Takahashi et al.\(^ {21}\) pointed out that the asymmetric stretching vibration in the electronic ground state was most efficient in promoting the fragmentation into channel (1). The predominant contribution of the anti-symmetric stretching vibration to the hot band excitation has been explained by large enhancement of the Franck-Condon
factors between the photoexcited state and the vibrationally excited level in the ground electronic state. The region II in Fig. 6 depicts the contribution of the O(\(1^D\)) formation via spin-forbidden channel (3), which is almost independent of the \(O_3\) temperature. Takahashi et al.\[^{21}\] suggested that the relative contribution from channel (3) to the O(\(1^D\)) quantum yield decreases from the value of 0.08 at 328 nm towards the shorter wavelength. The region III in Fig. 6 depicts the O(\(1^D\)) formation via channel (1) following excitation of \(O_3\) molecules in their ground vibrational level.

To verify the above-mentioned mechanism for O(\(1^D\)) formation, we present a quantitative model which accounts for the wavelength and temperature dependence of the O(\(1^D\)) quantum yield in the photolysis of \(O_3\), \(\Phi_{1D}(\lambda, T)\), based on the O(\(1^D\)) PHOFEX spectrum obtained in this study under the jet-cooled conditions. Model calculations for \(\Phi_{1D}(\lambda, T)\) have also been proposed by Adler-Golden et al.\[^{38}\] and Michelsen et al.\[^{28}\] In our new model, recent findings such as observation of the spin-forbidden channel (3) and propensity of the anti-symmetric vibration in the hot band excitation, are taken into account.

The partial cross section to produce O(\(1^D\)) atoms from \(O_3\) photolysis, \(\sigma_{1D}\), should be the summation of cross sections for each process I, II, and III, as depicted in Fig. 6:

\[
\sigma_{1D}(E_{ph}, T) = \sigma_{1D}^I(E_{ph}, T) + \sigma_{1D}^{II}(E_{ph}, T) + \sigma_{1D}^{III}(E_{ph}, T)
\]  \((9)\)

In Eq.(9), \(\sigma_{1D}\) is given as a function of photon energy, \(E_{ph}\), and gas temperature, \(T\). The jet-cooled O(\(1^D\)) PHOFEX spectrum obtained in the present study (Fig. 3) should be very close to the PHOFEX spectrum at \(T_{rot} = 0\) [K], that is, \(\sigma_{1D}^{III}(E_{ph}, T = 0)\). This is because that in the present experiments the rotational temperature of parent \(O_3\) molecules is as low as 3 K and the vibrational temperature is also low in the supersonic beam conditions\[^{34}\]. Since the vertical scale of the O(\(1^D\)) PHOFEX spectrum in Fig. 3 is relative, the absolute scale is given by multiplying a sensitivity factor to the spectrum measured;
\[
\sigma_{1D}^{\text{III}}(E_{\text{ph}}, T = 0) = s_{1D} \times Y_{1D}(E_{\text{ph}}, T = 0),
\]  
(10)

where \( Y_{1D}(E_{\text{ph}}, T = 0) \) is the jet-cooled PHOFEX spectrum for \( \text{O}(^1\text{D}) \) shown in Fig. 3.

Next, we calculate the hot-band cross sections, \( \sigma_{1D}^{\text{I}}(E_{\text{ph}}, T) \), from the \( \sigma_{1D}^{\text{III}}(E_{\text{ph}}, T = 0) \) derived above. The rotational and vibrational energies in a parent \( \text{O}_3 \) molecule are assumed to be equivalent to the increase of the photolysis photon energy. The contribution of the \( \text{O}(^1\text{D}) \) production from the rotationally excited but vibrationally cold \( \text{O}_3, \sigma_{1D}^{\text{III}}(E_{\text{ph}}, T) \), is calculated by convoluting the cross section \( \sigma_{1D}^{\text{III}}(E_{\text{ph}}, T = 0) \) with the rotational distribution function, \( P_{\text{rot}} \);

\[
\delta_{1D}^{\text{III}}(E_{\text{ph}}, T) = \sum_{E_{\text{rot}}} \delta_{1D}^{\text{III}}(E_{\text{ph}} + \delta_{\text{rot}} E_{\text{rot}}, T = 0) \cdot P_{\text{rot}}(E_{\text{rot}}, T),
\]  
(11)

where \( E_{\text{rot}} \) is the rotational energy of the parent \( \text{O}_3 \), and \( \alpha_{\text{rot}} \) is the fraction of rotational energy which is effective in overcoming the energy threshold for channel (1). The physical quantity of \( \alpha_{\text{rot}} \) is restricted to the range 0-1.\(^{39}\) For \( P_{\text{rot}} \) the normalized classical expression is assumed,

\[
P_{\text{rot}}(E_{\text{rot}}, T) = (E_{\text{rot}})^{1/2} \cdot T^{-3/2} \cdot \exp\left( -\frac{E_{\text{rot}}}{kT} \right),
\]  
(12)

where \( k \) is Boltzmann constant. Then, the effects of vibrational excitation in the hot-band cross sections are included by taking the vibrational energies, vibrational distribution function, and Franck-Condon factors into account;

\[
\delta_{1D}^{\text{I}}(E_{\text{ph}}, T) = \sum_{E_{\text{vib}}} f_v \cdot \sigma_{1D}^{\text{III}}(E_{\text{ph}} + E_{\text{vib}}, T) \cdot P_{\text{vib}}(E_{\text{vib}}, T),
\]  
(13)

where \( f_v \) is a ratio of the Franck-Condon factors between vibrationally hot and cold band excitations, FCF(v") / FCF(v"=0). The ratios \( f_v \) are given as linear functions of \( E_{\text{ph}} \). The \( P_{\text{vib}}(E_{\text{vib}}, T) \) is the vibrational distribution function at a temperature \( T \), which is given by the Boltzmann function. Since the contribution of antisymmetric vibration is predominant in the hot band excitation, the vibrational levels of \( v'' = 1 \) (\( E_{\text{vib}} = 1042 \text{ cm}^{-1} \)) and \( v'' = 2 \) (\( E_{\text{vib}} = 2084 \text{ cm}^{-1} \)) are taken into account.
The fundamental frequency of the antisymmetric vibration of O₃ in the electronic ground state was taken from the paper by Barbe et al.⁴⁰ The contributions of \( v' \geq 3 \) are ignored because of the small populations in the vibrational levels even at room temperatures. Consequently, we obtain the partial cross sections for region I in Fig. 6, \( \sigma_{1D}^I(E_{ph}, T) \).

Figure 7a is the result of the present model calculations giving the partial cross sections in arbitrary units for O(\(^1\)D) formation in the photolysis of O₃ between 305 and 329 nm. The solid line in Fig. 7a indicates the partial cross sections for rotationless (\( T_{rot} = 0 \) [K]) and vibrationless (\( v'' = 0 \)) O₃ molecule in arbitrary units, that is, \( Y_{1D}^{III}(E_{ph}, T=0) \). The dotted line represents the cross sections for O(\(^1\)D) formation from the rotationally excited and vibrationally cold O₃ molecules, which is the result of the convolution of the rotational excitation function at room temperature (eq.(12)) to the cross sections from rotationally and vibrationally cold O₃ molecules. The broken line is the hot-band partial cross sections calculated for O₃ molecules with \( v''=1 \) and \( T_{rot} = 295 \) K.

The partial cross sections for the O(\(^1\)D) production via the spin-forbidden channel (3), \( \sigma_{1D}^{II}(E_{ph}, T) \), which is depicted as region II in Fig. 6, are calculated. Experimental studies showed that the O(\(^1\)D) formation via channel (3), \( \Phi_{1D}^{II} \), gradually decreases from the value of 0.08 at 328 nm toward the shorter photolysis wavelength. The region II cross sections in the model calculations are thus given by multiplying the total O₃ absorption by the region II O(\(^1\)D) quantum yield \( \Phi_{1D}^{II} \) reported in the experimental study of Takahashi et al.\(^{21} \). Excitation energy dependent values for \( \Phi_{1D}^{II} \) in the model calculations are given by the linear function so that it is to be 0.08 at 329 nm and it decreases toward the shorter photolysis wavelength. The effect of the temperature on the region II cross sections \( \sigma_{1D}^{II}(E_{ph}, T) \) is neglected in the model calculations, since the region II O(\(^1\)D) quantum yield \( \Phi_{1D}^{II} \) has been found to be almost independent of the temperature by several experimental studies.\(^{20-22} \).
As a result, we obtain the partial cross sections for O(1D) production, $\sigma_{1D}(E_{ph}, T)$ in Eq. (9). The parameters used in the model calculations are summarized in Table III. Figure 7b shows the resultant O(1D) cross sections which are calculated with this model for 295 (thick line) and 227 K (thin line). The absorption cross sections for parent O$_3$ at 295 and 228 K $^7$ are also plotted for comparison, by thick and thin lines, respectively. Applying the modeled cross sections of $\sigma_{1D}(E_{ph}, T)$ to Eq. (7), we can derive the wavelength and temperature dependent quantum yield of the O(1D) production in the O$_3$ photolysis. Figure 8 shows the comparison of the model calculation results with the experimental results presented by Takahashi et al.$^{21}$ The model calculations well reproduce the experimental results for the O(1D) quantum yield values over the 305 - 329 nm range both at 227 and 295 K. The results of the present model calculations quantitatively confirm the mechanisms for the O(1D) formation processes (Fig.6) suggested from the experimental studies by Takahashi et al. $^{21}$

**Conclusion**

The PHOFEX spectra for both O(1D) and O(3P) fragments produced from the photodissociation of O$_3$ in the wavelength range of 296 - 316 nm are measured under jet-cooled and room temperature conditions. The PHOFEX spectra for O(3P) taken under jet-cooled and room temperature conditions do not suddenly decrease even at the wavelengths shorter than the thermodynamic threshold wavelength of the O(1D) + O$_2(a^1\Delta_g)$ dissociation at 309.44 nm. This suggests the presence of the exit barrier along the O-O$_2$ dissociation coordinate in the $^1B_2$ photoexcited electronic state of O$_3$. The sharp peaks are observed in both PHOFEX spectra for O(1D) and O(3P), which may be attributable to the long lifetimes of the quasi-bound levels between the thermodynamic threshold and the barrier top. The PHOFEX spectrum for O(3P) at 295 K provides the accurate O(1D) quantum yield values between 297 and 316 nm. The O(1D) quantum
yields between 297 and 305 nm are almost constant and obtained to be about 0.89. This value is in good agreement with the recent report by Talukdar et al. and is smaller than the NASA/JPL recommendation. The quantitative model calculations for the O(1D) formation are presented to explain the temperature and wavelength dependence of the O(1D) quantum yield between 305 and 329 nm, which is based on the dissociation mechanisms presented by Takahashi et al.\textsuperscript{21} The model includes the contributions of the spin-forbidden process (channel (3)) and thermal excitation in the vibrational and rotational states of O\textsubscript{3} molecules in the electronically ground state. The results of the model calculation well reproduce the O(1D) quantum yields obtained experimentally.

Acknowledgement.

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Table I. Fine structure branching ratios for the oxygen atom $\text{O}(^3\text{P}_j)$ from $\text{O}_3$ photolysis at various photolysis wavelengths.

<table>
<thead>
<tr>
<th>$\lambda$ $^a$</th>
<th>$T$ $^b$</th>
<th>Population $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$j = 2$</td>
</tr>
<tr>
<td>297</td>
<td>295</td>
<td>0.64 ± 0.03</td>
</tr>
<tr>
<td>305</td>
<td>295</td>
<td>0.63 ± 0.02</td>
</tr>
<tr>
<td>310</td>
<td>295</td>
<td>0.63 ± 0.02</td>
</tr>
<tr>
<td>305 $^d$</td>
<td>227</td>
<td>0.60 ± 0.02</td>
</tr>
<tr>
<td>308 $^e$</td>
<td>295</td>
<td>0.65 ± 0.02</td>
</tr>
<tr>
<td>Statistical $^f$</td>
<td></td>
<td>0.56</td>
</tr>
</tbody>
</table>

a. Photolysis wavelength in units of nm.
b. Sample gas temperature in units of K.
c. Normalized populations.
d. Reference 21.
e. Reference 16.
f. Degeneracy ratios, $2j + 1$
Table II. O(1^D) quantum yields from the photolysis of O₃ in the wavelength range of 295 – 308 nm at 295 K.

<table>
<thead>
<tr>
<th>λ (nm)²</th>
<th>This work b</th>
<th>Talukdar et al. c</th>
<th>NASA/JPL d</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>-</td>
<td>0.91 ± 0.01</td>
<td>0.95</td>
</tr>
<tr>
<td>297</td>
<td>0.89 ± 0.02</td>
<td></td>
<td>0.95</td>
</tr>
<tr>
<td>298</td>
<td>0.88 ± 0.02</td>
<td>-</td>
<td>0.95</td>
</tr>
<tr>
<td>299</td>
<td>0.89 ± 0.02</td>
<td>-</td>
<td>0.95</td>
</tr>
<tr>
<td>300</td>
<td>0.89 ± 0.02</td>
<td>-</td>
<td>0.95</td>
</tr>
<tr>
<td>301</td>
<td>0.90 ± 0.01</td>
<td>0.88 ± 0.01</td>
<td>0.95</td>
</tr>
<tr>
<td>302</td>
<td>0.90 ± 0.01</td>
<td>0.85 ± 0.02</td>
<td>0.95</td>
</tr>
<tr>
<td>303</td>
<td>0.90 ± 0.01</td>
<td>0.87 ± 0.09</td>
<td>0.95</td>
</tr>
<tr>
<td>304</td>
<td>0.89 ± 0.01</td>
<td>0.88 ± 0.09</td>
<td>0.95</td>
</tr>
<tr>
<td>305</td>
<td>0.90 ± 0.01</td>
<td>0.89 ± 0.10</td>
<td>0.95</td>
</tr>
<tr>
<td>306</td>
<td>0.88 ± 0.01</td>
<td>0.85 ± 0.07</td>
<td>0.91</td>
</tr>
<tr>
<td>307</td>
<td>0.84 ± 0.01</td>
<td>0.85 ± 0.10</td>
<td>0.85</td>
</tr>
<tr>
<td>308</td>
<td>0.79</td>
<td>0.79 ± 0.02</td>
<td>0.74</td>
</tr>
</tbody>
</table>

a. Photolysis wavelength

b. Determined from the PHOFEX spectrum for O(^3P) measured in this study, by using 0.79 at 308
nm as a reference value (see text). Uncertainties of the values at 297 – 307 nm do not include that of the reference value.

c. Taken from ref. 22. It has been reported that the O(\(^1\)D) yield value is 0.89 ± 0.02 between 289 and 305 nm, almost independent of temperature (203-320 K)

d. NASA/JPL recommendation for atmospheric modeling (ref.27)
Table III. Parameters used in our physical model calculations for the wavelength and temperature dependent quantum yield for O(1D) production from the ultraviolet photolysis of O₃ in the wavelength range of 305 - 329 nm.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{th}$</td>
<td>$32316 \text{ cm}^{-1} (= 309.44 \text{ nm})$</td>
</tr>
<tr>
<td>$f_{v''=1}$</td>
<td>$2$ at $33333 \text{ cm}^{-1} (= 300 \text{ nm})$ and $12 \pm 2$ at $30395 \text{ cm}^{-1} (= 329 \text{ nm})$, with the linear dependence on $E_{ph}$</td>
</tr>
<tr>
<td>$f_{v''=2}$</td>
<td>$60 \pm 20$</td>
</tr>
<tr>
<td>$\alpha_{rot}$</td>
<td>$0.65 \pm 0.1$</td>
</tr>
<tr>
<td>$\sigma_{1D II}$</td>
<td>$\sigma_{abs} \times \Phi_{1D}^{SF}$, where $\Phi_{1D}^{SF}$ is $0.08$ at $30395 \text{ cm}^{-1} (= 329 \text{ nm})$ and $0.02$ at $32316 \text{ cm}^{-1} (= 309.44 \text{ nm})$, with the linear dependence on $E_{ph}$</td>
</tr>
</tbody>
</table>

a. Threshold energy dissociating into O(1D) + O$_2$($a^1\Delta_g$), which corresponds to the wavelength of 309.44 nm (ref. 26). This value was fixed in the model calculations.

b. Ratio of Frank-Condon factors, FCF($v''=1$)/FCF($v''=0$), of the optical transitions from the vibrationless and the vibrationally excited levels in the ground electronic state, which was given by the linear function so that they are to be $2$ and $12 \pm 2$ at $33333 \text{ cm}^{-1} (= 300 \text{ nm})$ and $30395 \text{ cm}^{-1}(= 329 \text{ nm})$ (see text).

c. Same as b, but for FCF($v''=2$)/FCF($v''=0$). Given by the constant.

d. Fraction of rotational energy effective in overcoming the threshold into the O(1D) + O$_2$($a^1\Delta_g$) products (see text).
e. The partial cross sections for forming O($^1D$) atoms via the spin-forbidden O($^1D$) + O($^3Σ_g^-$) channel, which were obtained by multiplying the O$_3$ absorption by the photolysis energy dependent O($^1D$) quantum yield (see text). The O($^1D$) quantum yield was given by the linear function so that it is to be 0.08 at 30395 cm$^{-1}$ (= 329 nm) and to be 0.02 at 32316 cm$^{-1}$ (= 309.44 nm).
Figure captions

Figure 1 A schematic section through the approximate low-lying potential energy surfaces (PES) of O₃ along a dissociation coordinate R(O₂-O). The potential curve diagram presented by Hay et al.⁸ is modified. A broken curve is added as the potential curve representing the triplet state which is responsible for the spin-forbidden formation of O(^1D). Dotted curve is also added for the O(^1D) + O₂(^1Δg) formation without an exit energy barrier (see text). Symmetry representations are shown in Cᵥ point group.

Figure 2 Photofragment excitation (PHOFEX) spectrum for O(^3P) atoms produced from the photolysis of O₃ taken under flow conditions at 295 K. The PHOFEX spectrum was obtained by scanning the photolysis laser wavelength between 297 and 314 nm while monitoring the vuv-LIF intensity of O(^3P) atoms at 130 nm. The PHOFEX spectrum was corrected for intensity variations of the photolysis and probe lasers. Photoabsorption spectrum of O₃ molecules at 295 K is also shown in the upper panel for comparison, which is reported by Malicet et al.⁷ Broken curve in the lower panel represents the virtual PHOFEX spectrum for O(^3P) (see text).

Figure 3 Comparison of photofragment excitation (PHOFEX) spectra taken under room temperature (295 K) and supersonic free-jet conditions for both O(^1D) and O(^3P) atoms produced from the photolysis of O₃. The PHOFEX spectra were obtained by scanning the photolysis laser wavelength while monitoring the LIF intensity of O(^1D) or O(^3P) atoms. Spectra were corrected for intensity variations of the photolysis and probe lasers. A vertical broken line indicates the thermodynamic threshold for the dissociation channel to O(^1D) + O₂(^1Δg) (=309.44 ± 0.03 nm ²⁶).

Figure 4 Detailed PHOFEX spectra of O(^1D) and O(^3P) atoms from the photolysis of O₃
under jet-cooled conditions in the wavelength range of 306 - 310 nm. Spectra were corrected for
the intensity variations of the photolysis and probe lasers.

**Figure 5** Quantum yields of the O($^1D$) formation from the ultraviolet photolysis of O$_3$ at
room temperature (295 K) as a function of the photolysis wavelength. The O($^1D$) quantum yields
are obtained from the O($^3P$) PHOFEX spectrum in Fig. 2, using eq. (7) obtained in this study for
297 - 314 nm (see text). Broken line shows the NASA/JPL recommendation $^{27}$ for use in the
stratospheric modeling. Open triangles indicate the recent experimental results by Talukdar et al. $^{22}$
Filled circle at 308 nm indicates the reference value point (= 0.79). A vertical broken line indicates
the thermochemical threshold for channel of O($^1D$) + O$_2$(a$^1Δ_g$).

**Figure 6** Schematic diagram depicting the contributions made by the various dissociation
processes contributing to the quantum yield spectra for O($^1D$) atoms from O$_3$ photolysis in the
wavelength range 305 - 328 nm. This figure is taken from ref. 21. The solid curve is the
quantum yield spectrum obtained experimentally at 295 K, while the dashed curve is that obtained
at 227 K. Region I (shaded) indicates the contribution from the hot band excitation leading to
O($^1D$) + O$_2$(a$^1Δ_g$) [channel (1)] at 295 K. Region II (black) represents the contribution from the
spin-forbidden process leading to O($^1D$) + O$_2$(X$^3Σ_g^-$) [channel (2)]. Region III corresponds to the
O($^1D$) formation following excitation of vibrationless parent molecules and dissociation to O($^1D$) +
O$_2$(a$^1Δ_g$) [channel (1)].

**Figure 7** (a) The cross sections for O($^1D$) formation from the photolysis of O$_3$, which are
obtained by the physical model calculations in this study (see text). Solid line is the yield
spectrum of the O($^1D$) formation following the photoexcitation of the vibrationless ($v'' = 0$) and
rotationless \( (T_{rot} = 0) \) \( \text{O}_3 \) molecules, which is assumed to be proportional to the jet-cooled \( \text{O}^1\text{D} \) PHOFEX spectrum shown in Fig.3. Dotted line is the \( \text{O}^1\text{D} \) yield spectrum calculated for the \( v'' = 0 \) state of \( \text{O}_3 \) with thermal rotational excitation at 295 K. Broken line is the yield spectrum simulated for the \( v_3'' = 1 \) state of \( \text{O}_3 \) with \( T_{rot} = 295 \) K. (b) Partial absorption cross section spectra \( (\sigma_{1\text{D}}) \) for the \( \text{O}^1\text{D} \) formation from the \( \text{O}_3 \) photolysis at 295 K (thick line) and 228 K (thin line), which are calculated from the spectra shown in (a) using the fitting parameters listed Table III. Total absorption cross section spectra \( (\sigma_{abs}) \) measured by Malicet et al.\(^7\) are also shown at 295 K (thick line) and 228 K (thin line).

Figure 8: Quantum yields of the \( \text{O}^1\text{D} \) formation from the uv photolysis of \( \text{O}_3 \) at 295 K and 227 K as functions of the photolysis wavelength. Solid lines are the results of the model calculations. Open circles and rhombuses are experimental results at 295 K and 227 K, respectively, which are reported by Takahashi et al.\(^{21}\)
References


Fig. 1

Energy

O\textsuperscript{2} - O bond length

$^1\text{B}_2$

$^2\text{A}_1$

$X^1\text{A}_1$

$O(^1\text{D}) + O_2(^2\text{A}_1)$

$O(^1\text{D}) + O_2(^3\Sigma_g^-)$

$O(^3\text{P}) + O_2(^3\Sigma_g^-)$
Fig. 2

O\textsubscript{3} absorption
295 K

O\textsuperscript{3}(\textsuperscript{3}P) PHOFEX
295 K
Fig. 3
Fig. 4

O$_3$ absorption (218 K)

O($^1$D) jet

O($^3$P) jet
Fig. 5

$O(^1D) + O_2(^1\Delta_g)$

$O(^1D)$ Quantum Yield

$295 \text{ K}$

- Our group
- Talkudar et al.
- NASA/JPL '97
Fig. 6

O(\(^1\text{D}\)) Quantum yield

Photodissociation wavelength / nm

Fig. 6
Fig. 7

(a) Cross Section / arb.units

(v'' = 0)  (v'' = 1)

(b) Cross Section / 10^{-19} cm^2 molecule^{-1}

σ_{abs}

σ_{1D}

Wavelength / nm
Fig. 8